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TO: Mr. F.J. Kee
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LASER INDUCED FLUORESCENCE OF IODINE

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A laser induced fluorescence (LIF) technique for the detection of iodine has been experimentally investigated as a potential on-line real-time monitor of iodine-129 in nuclear fuel reprocessing plants. To avoid interference by NO_2, attention was focused on the fluorescence excited by an ultraviolet laser operating near 250 nm, whose design and construction are described. Measurements of the LIF spectrum of iodine under these conditions yielded no detectable signals. Methods of enhancing the signal strength are considered, along with alternative laser monitoring schemes.

1.0 INTRODUCTION

As part of Ontario Hydro's technical assistance to AECL in nuclear fuel reprocessing, discussions were held with members of the Fuel Recycle Branch of Whiteshell Nuclear Research Establishment (WNRE) to identify areas where the overlap between the Science Section's technical expertise and WNRE's research needs could be maximized/1/. One such area is the laser-based monitoring of radioactive iodine-129, a nuclear fission product which is released as a gas in the course of fuel reprocessing/2/. Measurements of iodine-129 concentration are required before and after filtering, with typical concentrations ranging from 30 ppm before the filter to 100 ppb after filtering.

Since conventional counting techniques are impractical due to the low activity of iodine-129, attention has turned to optical methods, which are well suited to on-line, real-time monitoring applications. Earlier work by Vikis at WNRE/3/ explored several laser-based techniques for detecting iodine, including optical absorption and laser induced fluorescence (LIF) using a helium-neon (He-Ne) laser. The best sensitivity was obtained with an intracavity LIF method which yielded a detection limit of 1 ppb. However, none of these techniques is adequate in the presence of NO_2, which is present at the 2 to 3% level and which also fluoresces under He-Ne laser excitation.

Similar problems were encountered by researchers in the US. A group at Naval Research Laboratory developed a prototype iodine-129 detector using LIF excited by an isotopic

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helium-neon laser (^{3}He-^{22}Ne)/4/. This gave a detection limit of 10 ppb but again the presence of NO_2, in this case at the 0.3% level, represented a serious interference with iodine-129 measurements at concentrations below 300 ppb.

The aim of the present research was to again explore LIF as a detection technique, since it represents a highly sensitive method which lends itself to remote, on-line monitoring, but to avoid NO_2 interference by selecting an excitation wavelength where I_2 fluoresces but NO_2 does not. Since there was reason to believe that I_2 would fluoresce over most of the visible and ultraviolet spectral range, the study focussed on the ultraviolet region near 250 nm where NO_2 fluorescence is expected to be minimal. This is because NO_2 has a very low absorption coefficient at this wavelength and absorption is a prerequisite for fluorescence.

This report describes the design of the tunable ultraviolet laser system used to generate the required output near 250 nm and the use of this source to investigate iodine fluorescence. Because these preliminary experiments did not yield a detectable signal, fluorescence measurements were subsequently made using visible excitation (632.8 nm) to verify that the fluorescence cell and detection system were functioning properly. Finally, the report considers possible methods of enhancing the ultraviolet LIF signal as well as alternative laser-based approaches which might be used to develop an iodine monitor.

2.0 ULTRAVIOLET LASER INDUCED FLUORESCENCE OF IODINE

2.1 Design of Laser System

The Quantel Nd:YAG pumped dye laser has a tuning range of 295 to 750 nm. Previous experience in our laboratory with extending the tuning range into the infrared using non-linear crystal mixing techniques/5/ proved useful in the present conversion into the ultraviolet using similar methods.

Figure 1 is a schematic of the ultraviolet laser design. The Nd:YAG laser operates at a fixed wavelength of 1.06 μm which is frequency doubled to 532 nm. The remaining 1.06 μm beam is optically delayed using a set of mirrors and the appropriate polarization for mixing is selected using quarter wave plates. The green 532 nm beam pumps the dye laser (rhodamine 640 dye) to generate tunable output in the red near 654 nm which is frequency doubled to yield ultraviolet output near 327 nm. A glass filter rejects the 654 nm beam and the 327 nm and 1.06 μm beams are combined in a crystal of KDP (potassium dihydrogen phosphate). By angle tuning this crystal, it is possible to generate output near 250 nm by the process of sum frequency mixing; ie, 1.06 μm ($\equiv$9,434 cm^{-1}) + 327 nm ($\equiv$30,566 cm^{-1}) $\rightarrow$ 250 nm ($\equiv$40,000 cm^{-1}). The three beams emerging from the mixing crystal are spatially separated by a prism and the 250 nm beam, whose wavelength is adjustable by tuning the dye laser, is passed into the iodine fluorescence cell. In this way, pulse energies of 0.5 to 1 mJ were generated in the ultraviolet.

2.2 Iodine Fluorescence Measurements

An all-quartz cell consisting of three quartz windows fused onto the cell body was constructed for these measurements/6/. This design is preferable to the simpler approach of sealing windows onto the cell because iodine vapor attacks most sealing compounds/7/.

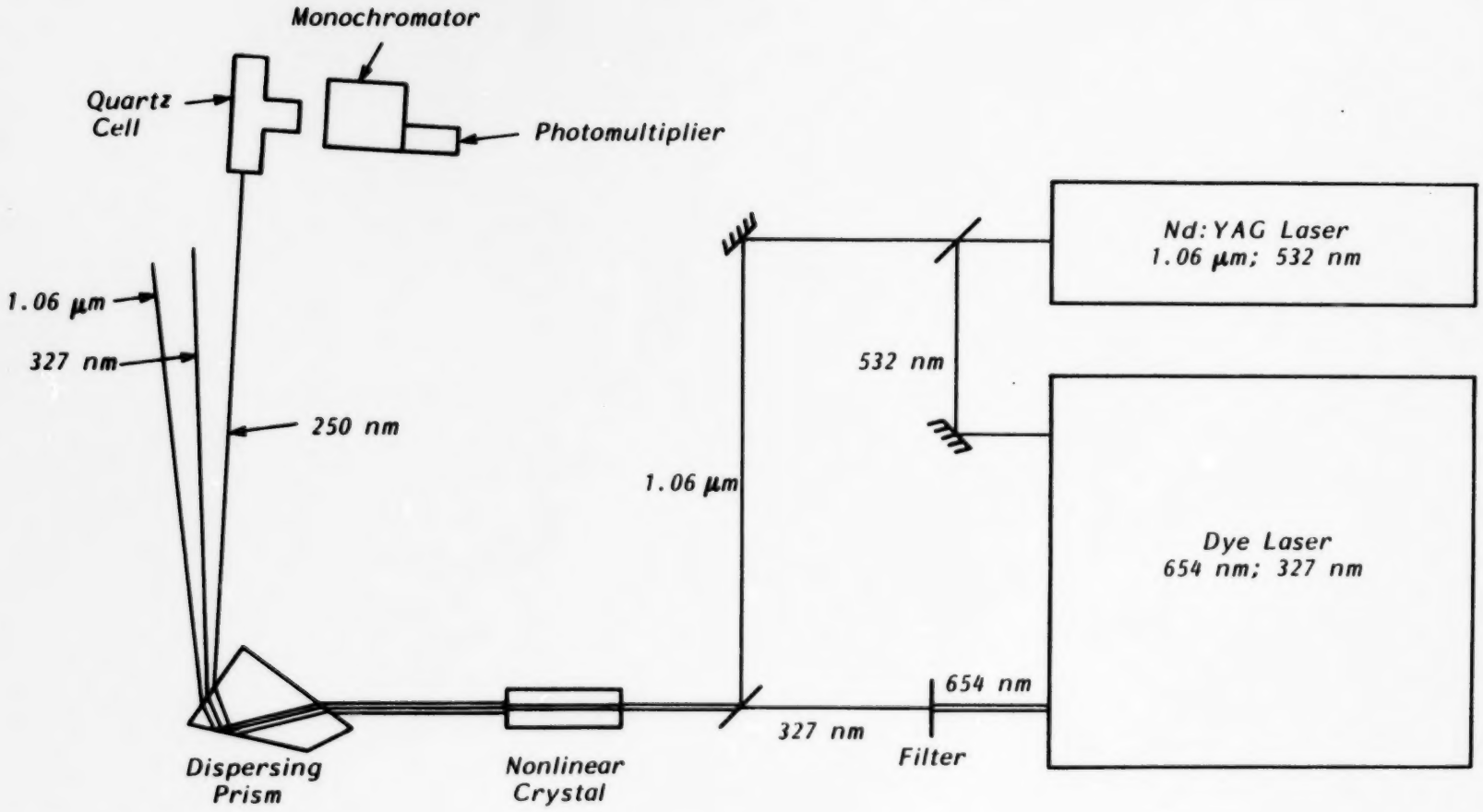

FIGURE 1

GENERATION OF TUNABLE ULTRAVIOLET OUTPUT USING NONLINEAR MIXING

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Iodine crystals were placed in a finger attached to the bottom of the fluorescence cell. At room temperature (23°C) the vapor pressure of iodine, as calculated from an equation in reference 7, is 284 mtorr.

The iodine fluorescence passed through a window at 90° to the laser beam and was spectrally analyzed with a monochromator (Monospec) connected to a photomultiplier detector (Hamamatsu R446). The monochromator was scanned while recording the photomultiplier output on a strip chart recorder, using a lock-in amplifier to improve the signal to noise.

With the ultraviolet excitation the only signals detected were a sharp line at the excitation wavelength and a broad, featureless emission at higher wavelengths. These were ascribed to scattering and fluorescence, respectively, of the quartz input window which was transferred along the wall of the cell to the viewing window. It is certain that the observed fluorescence is not due to iodine since there was nc change in the measured spectrum when the iodine was removed from the path of the laser beam by freezing out with liquid nitrogen.

3.0 FLUORESCENCE OF IODINE USING VISIBLE LASER EXCITATION

In order to confirm that the lack of ultraviolet fluorescence signal was not caused by a problem with the fluorescence cell or the detection system, the measurement was repeated with a helium-neon laser at 632.8 nm as the source of excitation. Similar results were obtained using the dye laser tuned to this wavelength.

Figure 2 shows the fluorescence spectrum of iodine at 23°C under these conditions. The inset is a diagram of the iodine energy levels showing the origin of the various emission lines following population of the V=6 level by the exciting radiation at 632.8 nm. All of the expected lines are observed except for (6,13) which is too weak and (6,3) which is obscured by the strong scattering of the laser exciting line. These observations are entirely consistent with earlier measurements of the He-Ne laser excited fluorescence spectrum of iodine/3/.

4.0 FUTURE RESEARCH

4.1 Enhancement of Ultraviolet Fluorescence

There is one reference in the literature to earlier attempts to measure the fluorescence of iodine using excitation near 250 nm, in this case as provided by a low pressure mercury lamp/8/. In this investigation, fluorescence was only detected at high temperature (500°C) and a pressure of 100 torr and became intense only at atmospheric pressure (760 torr). Other studies of iodine fluorescence stimulated by vacuum ultraviolet excitation below 200 nm have demonstrated that the addition of a buffer gas increases the fluorescence intensity/9/.

These observations suggest that one promising approach to enhancing the fluorescence of iodine near 250 nm would be to add enough nitrogen buffer to bring the total pressure up to one atmosphere and to also operate at higher temperatures by enclosing the cell in an

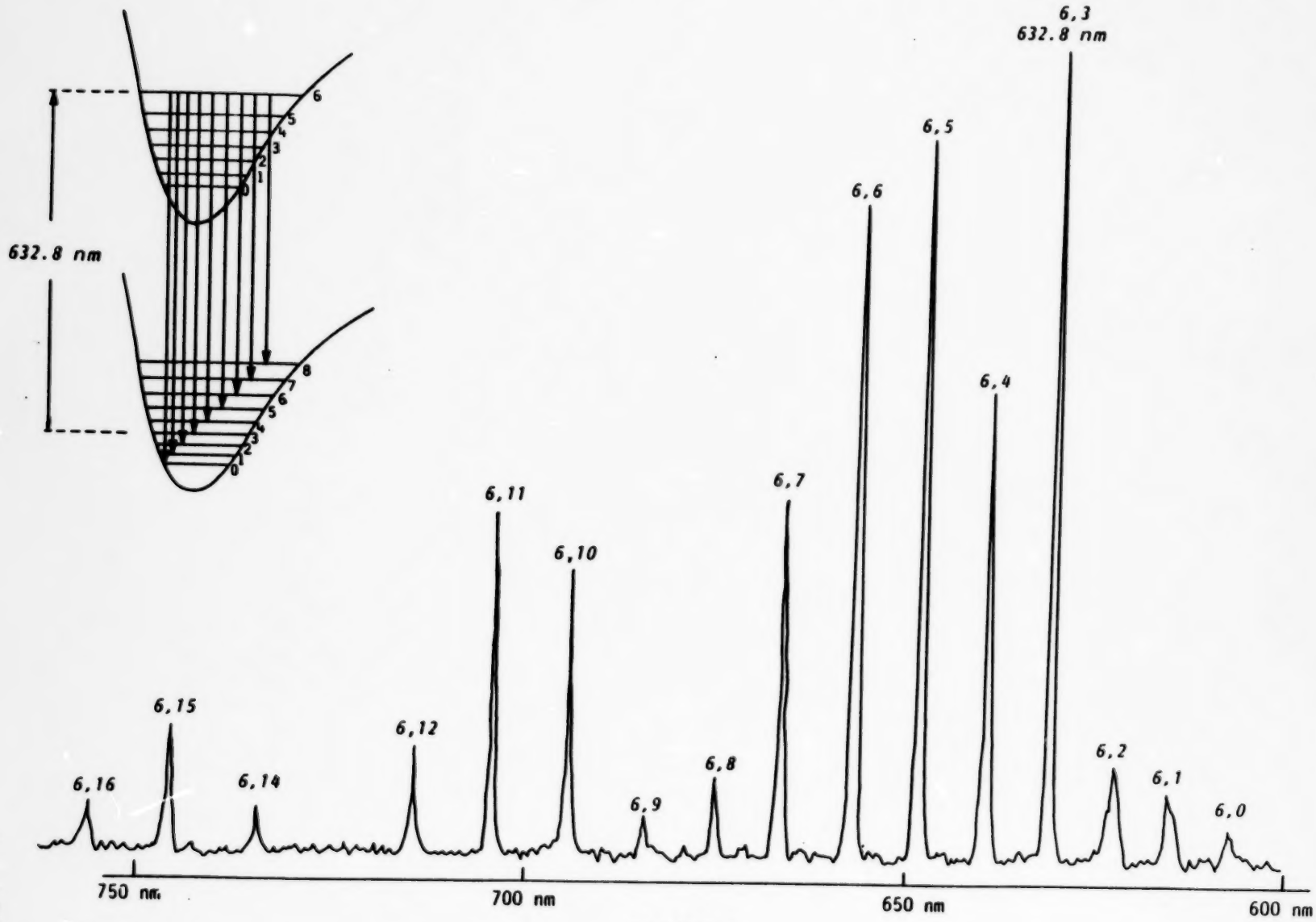

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FIGURE 2

LASER-INDUCED FLUORESCENCE SPECTRUM OF IODINE
WITH HELIUM-NEON LASER EXCITATION

oven. Another advantage of using the buffer gas is that it would make the experimental conditions more representative of the situation in a reprocessing plant where trace amounts of iodine would be present in an atmosphere of air.

4.2 Alternative Approaches

As mentioned above, the fluorescence of iodine has been observed under vacuum ultraviolet excitation, specifically using an argon fluoride (ArF) laser at 193 nm/9/. Since NO_2 is not expected to fluoresce in this spectral region, this represents one alternative approach that may be worth investigating. Excimer lasers such as ArF have undergone rapid development over the past several years and commercial units are currently available for US $20,000.

Another iodine detection scheme which we have considered is to use He-Ne laser excitation, for which the fluorescence of iodine has been well established, and to select a fluorescence emission line which does not overlap one of the NO_2 emission lines. This approach could work well as a monitor before the iodine filter, but would probably lack the sensitivity to be useful at the low iodine concentrations after filtering. It is estimated that, with the fluorescence intensities observed in Figure 2, the detection limit for iodine using a single line would be 40 ppm.

Finally, the technique of two photon spectroscopy has been considered as an alternative to laser induced fluorescence/2/. Research on this subject has been performed by J.R. Robins of the Science Section/7/ using two tunable dye lasers to populate an upper level in two steps and measuring the subsequent emission from this upper level. This method can be readily adapted to detect any of the isotopic forms of iodine and would probably have adequate sensitivity. While at first glance the cost of two lasers may seem prohibitive, there are compact nitrogen laser pumped dye lasers on the market for as little as US $5,000. It may also be possible to design the process so that both photons are generated by a single dye laser system.

CONCLUSION

The fluorescence of pure iodine as excited by ultraviolet light near 250 nm is too weak to be useful in iodine monitoring applications.

RECOMMENDATIONS

1. Methods of enhancing the ultraviolet fluorescence of iodine by the addition of a buffer gas and the use of higher temperatures should be investigated.

2. Alternative approaches which merit further experimental study are two photon spectroscopy and laser induced fluorescence using an argon fluoride laser at 193 nm.

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